

Coordination Chemistry of 2-(2'-Hydroxyphenyl)-2-benzoxazole with Gallium(III) and Aluminum(III): Two Uncommon Group 13 Metal Environments Stabilized by a Biologically Relevant Binding Group

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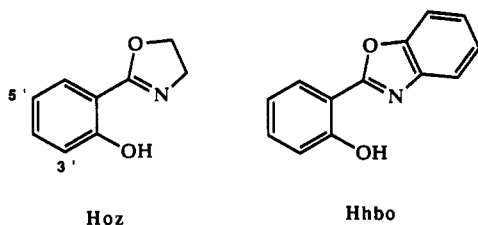
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The coordination chemistry of Ga(III) and Al(III) with 2-(2'-hydroxyphenyl)-2-benzoxazole (Hhbo) was investigated both in the solid state (X-ray crystallography) and in solution (^1H , ^{13}C , ^{27}Al NMR). These two group 13 metal ions exhibit different reactivities toward this bulky bidentate ligand leading with Ga(III) to the formation of Ga-(hbo)₃ (1) and [Ga(hbo)₂(O,O'-CH₃CO₂)] (2) complexes depending on the reaction conditions. With Al(III), the only complex formed is [Al(μ-OH)(hbo)₂]₂ (3). The Ga bis(ligand) acetate complex 2 (C₂₈H₁₉GaN₂O₆) crystallizes in the monoclinic space group C2/c with $a = 16.008(3)$ Å, $b = 10.621(2)$ Å, $c = 15.848(4)$ Å, $\beta = 115.85(1)^\circ$, $V = 2425(1)$ Å³, $Z = 4$, $R = 0.032$, and $R_w = 0.029$ for 2188 reflections ($I \geq 3\sigma(I)$). The dinuclear complex 3·4CH₃OH·H₂O (C₅₆H₅₂Al₂N₄O₁₅) crystallizes in the monoclinic space group P2₁/a with $a = 18.866(3)$ Å, $b = 14.332(3)$ Å, $c = 19.509(2)$ Å, $\beta = 91.51(1)^\circ$, $V = 5273(3)$ Å³, $Z = 4$, $R = 0.059$, and $R_w = 0.054$ for 4254 reflections ($I \geq 3\sigma(I)$). The structures were solved by Patterson (Ga complex) and direct (Al complex) methods and were refined by full-matrix least-squares procedures. The Ga complex 2 has a distorted octahedral geometry with the four O donor atoms defining the octahedral plane; the molecule possesses a crystallographically imposed C₂ axis of symmetry. 3 is a relatively rare example of a crystallographically characterized bis(μ-hydroxo)-bridged dimer, a hydrolysis species whose existence has been questioned in a number of potentiometric studies of aluminum complexation. The bridging geometry for 3 is as follows: Al...Al = 2.966(2) Å, Al-O(bridge) range = 1.870(4)–1.879(4) Å; Al-O-Al = 103.8(2), 104.6(2)°. The [Al₂(μ-OH)₂]⁴⁺ core is strictly planar, and there is a pseudo-2-fold rotation symmetry along the Al-Al axis, with oxazole N atoms *trans* to each other at either half of the molecule. The solution structure (in CDCl₃) is shown to be the same as that found in the solid state.

Introduction

Previously, we reported preparation and characterization of the first tris(ligand)metal complexes of group 13 (IIIA) metal complexes (Al, Ga, In) with a series of (3'- or 5'-substituted) ligands based on the naturally occurring binding group 2-(2'-hydroxyphenyl)-2-oxazoline (Hoz).¹ In a continuation of our

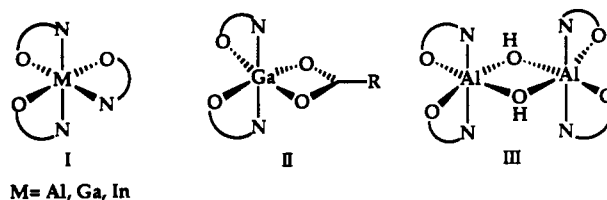


efforts to further this aspect of the coordination chemistry of group 13 metal ions, we describe herein the syntheses and solid state and solution characterizations of the Al and Ga complexes with a bulkier analog, 2-(2'-hydroxyphenyl)-2-benzoxazole (Hhbo).

In contrast to Hoz and its substituted analogs, which formed¹ stereochemically rigid *mer*-tris(ligand) complexes with both Al and Ga (Chart I, I), 2-(2'-hydroxyphenyl)-2-benzoxazole shows distinctly different reactivities toward these two metal ions under identical synthetic conditions affording two different and relatively rare structural motifs: [Ga(hbo)₂(O,O'-CH₃CO₂)] and [Al(μ-OH)(hbo)₂]₂ (Chart I, II and III).

The presence of oxo-bridged polynuclear Fe(III) complexes² involving carboxylato and/or hydroxo bridging ligands in a variety

Chart I



M = Al, Ga, In

of metalloenzymes has prompted the synthesis and X-ray structural characterization of a large variety of synthetic analogs⁵ with this binding motif; however, to our knowledge only two other examples of structurally characterized mononuclear Fe(III) or Ga(III) metal complexes involving a chelating carboxylate ligand have been reported to date.⁶ In both of these instances,⁷

(2) Structurally, Fe(III) (d^5) and Ga(III) (d^{10}) are quite similar; both have the same charge and similar ionic radii in six-coordinated complexes, 0.645 Å for Fe(III) compared to 0.620 Å for Ga(III).³ In addition, since neither have any crystal field stabilization and both have similar ionic radii, they both exhibit similar ligand-exchange rates.⁴

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(5) For reviews on oxo- and hydroxo-bridged iron complexes see: Lippard, S. J. *Angew. Chem., Int. Ed. Engl.* 1988, 27, 344. *Metal Clusters in Proteins*; Que, L., Jr., Ed.; ACS Symposium Series 372; American Chemical Society: Washington, DC, 1992. Que, L., Jr.; True, A. E. *Prog. Inorg. Chem.* 1990, 38, 98. Kurtz, D. M., Jr. *Chem. Rev.* 1990, 90, 585. Vincent, J. B.; Olivier-Lilley, G. L.; Averill, B. A. *Chem. Rev.* 1990, 90, 1447.

(6) It is worth mentioning that the X-ray structure of the oxidized form of ribonucleotide reductase (RRB2) at 2.2-Å resolution shows the coordination of an aspartate carboxylate (Asp 84) in a bidentate fashion to one of the Fe(III) atoms of the dinuclear iron center (Nordlund, P.; Sjöberg, B.-M.; Eklund, H. *Nature* 1990, 345, 593) and that human lactoferrin shows a bidentate carbonate bound to each iron center (Shongwe, M. S.; Smith, C. A.; Ainscough, E. W.; Baker, H. M.; Brodie,

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(1) Hoveyda, H. R.; Karunaratne, V.; Rettig, S. J.; Orvig, C. *Inorg. Chem.* 1992, 31, 5408.

pyrazolylborate-type ligands were employed as the sterically bulky ligand to effect the accommodation of the geometrically constraining chelating carboxylate which has a small bite angle of ca. 60°.

In the absence of other ligands, the Al(III) aquo ion, the "hardest" of the aquo ions commonly occurring in the environment and in biological systems,⁸ undergoes extensive hydrolysis (above pH 3) forming a variety of mononuclear and polynuclear species.⁹ In contrast to the sequentially formed mononuclear hydrolysis species, the formation of polynuclear species is less facile and highly concentration dependent. Earlier studies indicate that the three polynuclear species formed by Al³⁺ hydrolysis are [Al₂(μ-OH)₂]⁴⁺, [Al₃(μ-OH)₄]⁵⁺, and [Al₁₃O₄(μ-OH)₂₄]⁷⁺—the last being the most stable of the three.⁹ However, recent (potentiometric) investigations have suggested that the dimeric species [Al₂(μ-OH)₂]⁴⁺ does not occur to a significant extent¹⁰ unless stabilized by auxiliary ligands such as bridging carboxylate,¹¹ carbonate,^{10b,12} or phosphate.¹³ To date, four examples of Al complexes with a [Al₂(μ-OH)₂]⁴⁺ core have been structurally characterized: [Al(en)(OCH(CF₃)₂(μ-OH))₂] (en = ethylenediamine),¹⁴ [Al(H₂O)₂][Al₂(nta)₂(μ-OH)₂]OH·3H₂O (nta = nitrilotriacetate),¹⁵ the "basic aluminum sulfate", [Al₂(H₂O)₈(μ-OH)₂](SO₄)₂·2H₂O,¹⁶ and the binuclear cation [(ClAl(μ-OH)₂AlCl)·18-crown-6]²⁺.¹⁷ Therefore this work presents an instance where two uncommon group 13 metal coordination geometries have been stabilized in the presence of water by the same ligating moiety.

Experimental Section

Materials and Methods. All chemicals were reagent grade and were used as received: Ga(NO₃)₃·xH₂O (x ≈ 3), Al(NO₃)₃·9H₂O, and 2-(2'-hydroxyphenyl)-2-benzoxazolo (Aldrich). Water was deionized (Barnstead D8902 and D8904 cartridges) and distilled (Corning MP-1 Megapure still). The yields reported refer to the isolated yields.

Instrumentation. NMR spectra were recorded on Bruker AC-200E (¹H, 200 MHz), Varian XL-300 (¹H, 300 MHz), Bruker WH-400 (¹H, 400 MHz), or Bruker AMX-500 (¹H, 500 MHz; ¹³C, 125 MHz; ¹³C-¹H HETCOR) instruments. ¹H NMR data are reported as δ downfield from TMS (external reference) in CDCl₃ unless otherwise stated. Infrared spectra were recorded as KBr disks in the range 4000–400 cm⁻¹ on a Perkin-Elmer PE783 spectrophotometer and were referenced to polystyrene. Mass spectra were obtained with a Kratos MS 50 (electron-

impact ionization, EI) and Kratos Concept IIIH (fast-atom-bombardment, FAB, using a Cs ion gun at 12 kV). Appropriate isotope ratios for all Ga-containing compounds were observed; only the most intense peaks are listed. Melting points were measured on a Mel-Temp apparatus and are uncorrected. Analyses for C, H, and N were performed in this department on a Carlo Erba elemental analyzer.

²⁷Al NMR Spectroscopy. Spectra were recorded in CDCl₃ on a Varian XL-300 spectrometer operating at 78.16 MHz and accumulating 3500 transients with a pulse width of 15 μs and a spectral window of 37 kHz. All spectra were referenced to 0.20 M Al(ClO₄)₃ in 0.10 M HClO₄ with D₂O added as a lock signal, and downfield shifts are positive. The background correction was done for each spectrum by subtracting a spectrum run under identical conditions with the solvent.¹⁸

Metal Complex Syntheses. Tris[2-(2'-hydroxyphenyl)-2-benzoxazolo]gallium(III), Ga(hbo)₃ (1). To a solution of Hhbo (0.429 g, 2.03 mmol) in CH₃OH (90 mL) was added Ga(NO₃)₃·xH₂O in 10 mL of CH₃OH:H₂O (7:3) (0.274, 0.66 mmol), followed by 3.5 equiv of NaOH (1 M). The precipitate formed by the slow evaporation of the methanolic solution was washed with acetone and ether to afford a (combined) yield of 0.283 g (65%) as a light-pink solid, mp 284–285 °C. ¹H NMR (400 MHz, DMSO-*d*₆): 6.4–8.1 (series of overlapping multiplets). IR (cm⁻¹, KBr disk): 1610 (s, ν_{C-N}), 1560 (m, ν_{C-C}), 1542 (m, ν_{C-C}), 1480, 1440, 1345, 1260, 1160, 1070, 875, 810, 750, 640. MS (EI): *m/z* 211 (L⁺), 279 (ML⁺, ⁶⁹Ga), 489 (ML₂⁺, ⁶⁹Ga), 699 (ML₃⁺, ⁶⁹Ga). Anal. Calcd (found) for C₃₉H₂₄GaN₃O₆: C, 66.88 (66.86); H, 3.45 (3.38); N, 6.01 (5.89).

(Acetato-*O,O'*)bis[2-(2'-hydroxyphenyl)-2-benzoxazolo]gallium(III), [Ga(hbo)₂(*O,O'*-CH₃CO₂)] (2). To a solution of Hhbo (0.294 g, 1.39 mmol) in CH₃OH (110 mL) was added Ga(NO₃)₃·xH₂O (0.188 g, 0.45 mmol), followed by 3.3 equiv of NaOAc·3H₂O (0.246 g, 1.81 mmol) yielding 0.20 g (81%) of an orange-pink solid, mp 290–292 °C. This procedure also furnished X-ray-quality crystals over a period of 10 days. ¹H NMR (500 MHz): 1.71 (s, 3H), 6.87 (t, 2H, *J* = 6 Hz), 6.98 (d, 2H, *J* = 6 Hz), 7.40–7.50 (m, 6H), 7.64–7.68 (m, 2H), 8.00–8.10 (m, 4H). ¹³C NMR (125 MHz): 19.8, 110.6, 117.4, 119.2, 122.4, 125.0, 125.7 (2C, based on HETCOR), 128.1, 133.5, 135.6, 136.6, 148.3, 164.9, 165.9. IR (cm⁻¹, KBr disk): 1615 (s, ν_{C-N}), 1600 (m, ν_{C-C}), 1562 (m, ν_{C-C}), 1548 (m, ν_{C-C}), 1470, 1460, 1328, 1260, 1150, 1135, 1070, 870, 810, 750. MS (EI): *m/z* 211 (L⁺), 279 (ML⁺, ⁶⁹Ga), 338 (ML(OAc)⁺, ⁶⁹Ga), 489 (ML₂⁺, ⁶⁹Ga), 548 (ML₂(OAc)⁺, ⁶⁹Ga). Anal. Calcd (found) for C₂₈H₁₉GaN₂O₆: C, 61.24 (61.34); H, 3.49 (3.51); N, 5.10 (5.30).

Bis(μ-hydroxo)bis[2-(2'-hydroxyphenyl)-2-benzoxazolo]aluminum(III), [Al(μ-OH)(hbo)₂]₂(3). A preparation analogous to that for Ga(hbo)₃ with Al(NO₃)₃·9H₂O (0.123 g, 0.33 mmol), Hhbo (0.215 g, 1.02 mmol), and 3.5 equiv of NaOH (1 M) in 75 mL of CH₃OH:H₂O (80:1) yielded 60 mg (75% based on Al) of a light-pink crystalline solid, mp 273–274 °C. X-ray-quality crystals as 4CH₃OH·H₂O solvates were obtained by slow evaporation at room temperature over a period of 2 weeks. (These crystals were quite susceptible to solvent loss.) ¹H NMR (400 MHz): 6.6–8.1 (series of overlapping multiplets, 32H), 11.47 (s, 2H). IR (cm⁻¹, KBr disk): 3780–3300 (br, ν_{OH}), 1620 (s, ν_{C-N}), 1605 (m, ν_{C-C}), 1565 (m, ν_{C-C}), 1542 (s, ν_{C-C}), 1480, 1448, 1345, 1278, 1160, 1070, 1035, 1015 (δ_{br} OH), 880, 815, 745, 645. MS (+FAB): *m/z* 212 (L + H⁺), 447 (AlL₂⁺), 911 (Al₂(OH)L₄⁺), 928 (Al₂(OH)₂L₄⁺). Anal. Calcd (found) for C₅₂H₃₄Al₂N₄O₁₀: C, 67.24 (67.01); H, 3.69 (3.88); N, 6.03 (5.97). ²⁷Al NMR: 5 ppm (*W*_{1/2} = 2050 Hz).

X-ray Crystallographic Analyses of 2 and 3. Selected crystallographic data appear in Table I. The final unit-cell parameters were obtained by least squares on the setting angles for 25 reflections with 2θ = 37.6–43.0° for [Ga(hbo)₂(*O,O'*-CH₃CO₂)] **2**, and 26.2–53.4° for [Al(μ-OH)(hbo)₂]₂·4MeOH·H₂O **3**. The intensities of three standard reflections, measured every 200 reflections throughout the data collections, remained constant for both complexes. The data were processed¹⁹ and corrected for Lorentz and polarization effects and for absorption (empirical, based on azimuthal scans for three reflections).

The structure of the Ga complex, **2**, was solved by conventional heavy-atom methods, the coordinates of the Ga atom being determined from the Patterson function and those of the remaining non-hydrogen atoms from subsequent difference Fourier syntheses. The [Ga(hbo)₂(*O,O'*-CH₃CO₂)] molecule, **2**, has exact (crystallographic) C₂ symmetry. The structure of the Al complex **3** was solved by direct methods. The asymmetric unit of **3** contains the binuclear [Al(μ-OH)(hbo)₂]₂ molecule,

A. M.; Baker, E. N. *Biochemistry* **1992**, *31*, 4451). Furthermore, the structures that have been proposed for the diiron sites of methane monooxygenase (MMO) (Nordlund, P.; Dalton, H.; Eklund, H. *FEBS Lett.* **1992**, *307*, 257) and uteroferrin (Uf) (True, A. E.; Scarrow, R. C.; Randall, C. R.; Holtz, R. C.; Que, L., Jr. *J. Am. Chem. Soc.* **1993**, *115*, 4246) also entail a chelating carboxylate coordinated to one of the two iron centers.

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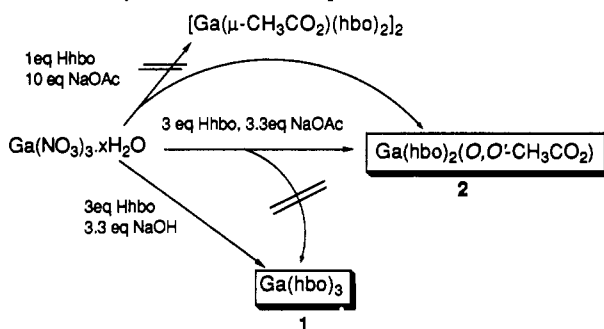
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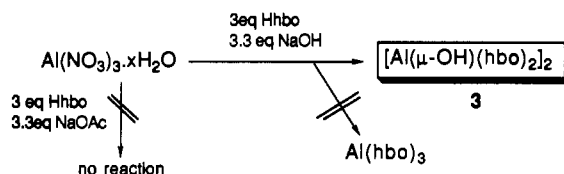
Table I. Selected Crystallographic Data for 2 and 3

compd	[Ga(hbo) ₂ (O,O'-CH ₃ CO ₂)] ₂ , 2	[Al(μ-OH)(hbo) ₂] ₂ ·4MeOH·H ₂ O, 3
formula	C ₂₈ H ₁₉ GaN ₂ O ₆	C ₅₆ H ₅₂ Al ₂ N ₄ O ₁₅
fw	549.19	1075.01
cryst system	monoclinic	monoclinic
space group	C2/c	P2 ₁ /a
a, Å	16.008(3)	18.866(3)
b, Å	10.621(2)	14.332(3)
c, Å	15.848(4)	19.509(2)
β, deg	115.85(1)	91.51(1)
V, Å ³	2425(1)	5273(3)
Z	4	4
ρ _{calc} , g/cm ³	1.504	1.354
T, °C	21	21
radiation	Mo	Cu
λ, Å	0.710 69	1.541 78
μ, cm ⁻¹	11.74	10.85
transm factors	0.82–1.00	0.96–1.00
R	0.032	0.059
R _w	0.029	0.054

Scheme I. Synthesis of Ga Complexes



Scheme II. Synthesis of the Al Complex

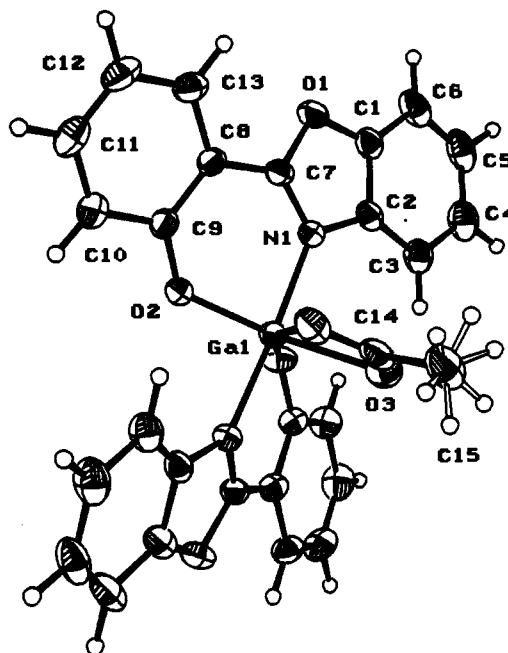


four methanol solvate molecules, and one water molecule. The five solvent molecule sites were fully occupied.

All non-hydrogen atoms of both structures were refined with anisotropic thermal parameters. The hydrogen atoms associated with the acetate ligand in 2 are 1:1 disordered about the crystallographic 2-fold axis. The hydrogen atoms associated with the methanolic oxygen atom O(13) and the water molecule O(15) in 3 were placed in difference map positions but were not refined. O–H hydrogen atoms associated with the remaining CH₃OH molecules in 3 could not be located and were not included in the model. All other hydrogen atoms in 2 and 3 were fixed in calculated positions (O–H/C–H = 0.98 Å, B_H = 1.2B_{bonded atom}). Secondary extinction corrections were applied in both cases, the final values of the extinction coefficients being 1.59(3) × 10⁻⁶ and 7.5(2) × 10⁻⁷, respectively, for 2 and 3. Neutral-atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref 20. Final atomic coordinates and equivalent isotropic thermal parameters appear in Table II, and selected bond lengths and bond angles for 2 and 3 appear in Tables III and IV, respectively. Complete tables of crystallographic data, bond distances, and bond angles, as well as tables of hydrogen atom parameters, anisotropic thermal parameters, torsion angles, intermolecular contacts, and least-squares planes, for both structures are included as supplementary material (see paragraph at the end of the paper).

Results and Discussion

Synthesis of Complexes. Schemes I and II summarize the synthetic routes to the Ga and Al complexes with Hhbo,

Figure 1. ORTEP view of [Ga(hbo)₂(O,O'-CH₃CO₂)].

respectively, outlining the different reactivities exhibited by this ligand with the two group 13 metal ions. For example, Ga(hbo)₃ was prepared from a methanolic solution containing a 1:3.1:3.5 ratio of Ga(NO₃)₃·xH₂O, Hhbo, and NaOH (1 M) in 65% (isolated) yield (Scheme I), whereas similar reaction conditions with Al(NO₃)₃·9H₂O produced a bis(μ-hydroxo)-bridged complex in 75% (isolated) yield (Scheme II). Evidently, the bulkiness of the hbo⁻ ligand together with the small size of the Al³⁺ cation (hexacoordinate ionic radius of 0.535 Å)² preclude the formation of an Al(hbo)₃ complex.

With NaOAc as base, complex 2 was isolated despite a stoichiometry amenable toward the formation of a tris(ligand)-metal complex. In fact, varying the stoichiometry (by using excess sodium acetate) to obtain a bis(μ-acetato)-bridged dimer also proved futile and 2 was isolated instead (*cf.* Scheme I). Therefore, insofar as these observations indicate, the hbo⁻ ligand shows a great propensity to forming [Ga(hbo)₂(O,O'-CH₃CO₂)] whether in the presence of excess Hhbo and/or excess sodium acetate. In contrast to Ga, no complexation occurred with Al when NaOAc was used as base; the unreacted ligand was recovered in nearly quantitative yield (*cf.* Scheme II).

Analyses for C, H, and N in each complex were consistent with the formulations given. The mass spectra of the complexes 1 and 2 were obtained in the EI mode and showed the expected ML'L₂⁺, ML₂⁺, ML'L⁺, ML⁺, and L⁺ fragmentation (for 1 L = L' = hbo⁻ and for 2 L' = OAc). In the Al complex, however, the molecular ion could only be detected in the FAB mode. The fragmentation pattern in 3 (Al₂(OH)₂L₄⁺) consisted of loss of a bridging hydroxo to form an (Al₂(OH)L₄⁺) species, followed by loss of the other bridging hydroxo and the subsequent fragmentation of the attached ligands.

A comparison of the IR spectral data of the complexes with those of Hhbo (not listed) revealed the most diagnostic feature to be the bathochromic shift of ν_{C=N} (ranging from 18 to 28 cm⁻¹). In 2, the stretching modes of the acetate CO₂⁻ (*ca.* 1560–1500 cm⁻¹) cannot be assigned unequivocally since they overlap with other modes such as the aromatic C=C stretch (*cf.* IR data for compound 1). Further, by analogy to the existing literature, the 1015-cm⁻¹ band in 3 was tentatively assigned as a bridge OH deformation band.²¹

Crystal Structures. Figure 1 shows the structure and atom-labeling scheme of [Ga(hbo)₂(O,O'-CH₃CO₂)]. The structure

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Table II. Final Atomic Coordinates (Fractional) and B_{eq} Values (\AA^2)^a

atom	x	y	z	B_{eq}	atom	x	y	z	B_{eq}
[Ga(hbo) ₂ (O,O'-CH ₃ CO ₂)] ₂									
Ga(1)	1/2	0.16271(4)	1/4	3.07(1)	C(6)	0.4808(2)	0.1587(3)	-0.1059(2)	5.3(1)
O(1)	0.36687(11)	0.12217(15)	-0.04084(10)	4.14(7)	C(7)	0.3771(2)	0.1246(2)	0.04855(15)	3.28(9)
O(2)	0.39785(10)	0.0612(2)	0.23183(10)	3.89(6)	C(8)	0.29946(14)	0.0917(2)	0.06739(15)	3.37(8)
O(3)	0.57095(12)	0.3344(2)	0.25985(11)	5.02(8)	C(9)	0.31504(14)	0.0626(2)	0.1593(2)	3.39(9)
N(1)	0.46044(11)	0.1557(2)	0.10949(11)	3.10(6)	C(10)	0.2373(2)	0.0277(3)	0.1739(2)	4.6(1)
C(1)	0.4532(2)	0.1531(2)	-0.0346(2)	4.0(1)	C(11)	0.1501(2)	0.0246(3)	0.1004(2)	5.3(1)
C(2)	0.5123(2)	0.1747(2)	0.05794(15)	3.43(9)	C(12)	0.1360(2)	0.0535(3)	0.0109(2)	5.1(1)
C(3)	0.6046(2)	0.2057(2)	0.0856(2)	4.5(1)	C(13)	0.2098(2)	0.0860(2)	-0.0065(2)	4.3(1)
C(4)	0.6329(2)	0.2127(3)	0.0147(2)	5.6(1)	C(14)	1/2	0.3951(4)	1/4	4.6(2)
C(5)	0.5722(2)	0.1895(3)	-0.0778(2)	5.8(1)	C(15)	1/2	0.5356(4)	1/4	6.7(2)
[Al(μ -OH)(hbo) ₂] ₂ ·4MeOH·H ₂ O									
Al(1)	0.18857(8)	0.41667(13)	0.30541(8)	3.44(9)	C(24)	-0.0229(4)	0.5841(6)	0.4233(4)	6.4(5)
Al(2)	0.27739(8)	0.55139(13)	0.23052(8)	3.41(9)	C(25)	0.0193(4)	0.6212(5)	0.4746(4)	6.8(5)
O(1)	0.1228(2)	0.2597(3)	0.1340(2)	4.7(2)	C(26)	0.0898(4)	0.5966(5)	0.4821(3)	5.2(4)
O(2)	0.2043(2)	0.2952(3)	0.3317(2)	3.9(2)	C(27)	0.3165(3)	0.6493(4)	0.3720(3)	3.6(3)
O(3)	0.2260(2)	0.5166(3)	0.5049(2)	5.0(2)	C(28)	0.3740(3)	0.6523(4)	0.4167(3)	3.9(3)
O(4)	0.0989(2)	0.4298(3)	0.3402(2)	4.2(2)	C(29)	0.3757(3)	0.6964(5)	0.4794(3)	5.1(4)
O(5)	0.4280(2)	0.5992(3)	0.3886(2)	4.3(2)	C(30)	0.3134(4)	0.7430(5)	0.4950(3)	5.5(4)
O(6)	0.3631(2)	0.5388(3)	0.1881(2)	4.0(2)	C(31)	0.2550(3)	0.7426(5)	0.4496(4)	5.4(4)
O(7)	0.1647(2)	0.5495(3)	0.0428(2)	5.1(2)	C(32)	0.2554(3)	0.6963(4)	0.3873(3)	4.5(3)
O(8)	0.2649(2)	0.6758(3)	0.2103(2)	4.0(2)	C(33)	0.4000(3)	0.5701(4)	0.3275(3)	3.6(3)
O(9)	0.1898(2)	0.5396(3)	0.2733(2)	3.3(2)	C(34)	0.4459(3)	0.5174(4)	0.2831(3)	3.7(3)
O(10)	0.2762(2)	0.4272(2)	0.2612(2)	3.3(2)	C(35)	0.4246(3)	0.5094(4)	0.2135(3)	3.8(3)
N(1)	0.1402(2)	0.3635(4)	0.2196(2)	3.5(2)	C(36)	0.4728(3)	0.4633(4)	0.1696(3)	4.6(3)
N(2)	0.2264(2)	0.4492(3)	0.4005(2)	3.6(2)	C(37)	0.5373(3)	0.4331(5)	0.1951(4)	5.4(4)
N(3)	0.3345(2)	0.5946(3)	0.3150(2)	3.4(2)	C(38)	0.5564(3)	0.4409(5)	0.2634(4)	5.5(4)
N(4)	0.2338(2)	0.5242(3)	0.1363(2)	3.5(2)	C(39)	0.5107(3)	0.4848(5)	0.3071(3)	4.7(3)
C(1)	0.0876(3)	0.3979(5)	0.1738(3)	4.0(3)	C(40)	0.2405(3)	0.4475(5)	0.0922(3)	4.0(3)
C(2)	0.0776(3)	0.3345(5)	0.1218(3)	4.5(4)	C(41)	0.1974(3)	0.4628(5)	0.0349(3)	4.9(4)
C(3)	0.0294(4)	0.3433(6)	0.0681(3)	6.1(4)	C(42)	0.1912(4)	0.4032(7)	-0.0204(3)	7.0(5)
C(4)	-0.0112(4)	0.4235(7)	0.0697(4)	7.0(5)	C(43)	0.2300(5)	0.3233(7)	-0.0153(4)	7.7(6)
C(5)	-0.0032(3)	0.4902(5)	0.1215(4)	6.0(4)	C(44)	0.2750(4)	0.3068(5)	0.0418(4)	6.6(5)
C(6)	0.0473(3)	0.4789(5)	0.1750(3)	4.9(4)	C(45)	0.2805(3)	0.3675(5)	0.0954(3)	4.9(4)
C(7)	0.1579(3)	0.2810(5)	0.1944(3)	3.7(3)	C(46)	0.1897(3)	0.5805(5)	0.1052(3)	4.1(3)
C(8)	0.2032(3)	0.2125(4)	0.2253(3)	3.8(3)	C(47)	0.1697(3)	0.6733(5)	0.1266(3)	4.2(3)
C(9)	0.2220(3)	0.2218(5)	0.2958(3)	3.8(3)	C(48)	0.2109(3)	0.7178(5)	0.1780(3)	4.3(4)
C(10)	0.2579(3)	0.1475(5)	0.3265(3)	5.2(4)	C(49)	0.1955(4)	0.8113(5)	0.1940(4)	5.4(4)
C(11)	0.2780(4)	0.0695(5)	0.2892(4)	6.4(5)	C(50)	0.1388(5)	0.8538(6)	0.1618(5)	7.5(5)
C(12)	0.2610(4)	0.0621(5)	0.2198(4)	6.4(5)	C(51)	0.0962(4)	0.8110(7)	0.1126(5)	7.6(5)
C(13)	0.2241(3)	0.1324(5)	0.1885(3)	5.1(4)	C(52)	0.1122(4)	0.7193(6)	0.0946(4)	6.2(4)
C(14)	0.2918(3)	0.4321(4)	0.4347(3)	3.8(3)	O(11)	0.0818(3)	0.6816(4)	0.2774(3)	8.5(3)
C(15)	0.2911(3)	0.4723(5)	0.4980(3)	4.4(3)	C(53)	0.0664(5)	0.7562(7)	0.3190(5)	9.6(6)
C(16)	0.3452(4)	0.4691(5)	0.5452(3)	5.6(4)	O(12)	-0.1057(3)	0.2132(4)	0.2598(4)	11.9(5)
C(17)	0.4034(4)	0.4189(6)	0.5253(3)	6.0(4)	C(54)	-0.0871(5)	0.2789(7)	0.2133(7)	13.7(9)
C(18)	0.4062(3)	0.3757(5)	0.4615(4)	5.4(4)	O(13)	0.3839(7)	0.8253(11)	0.2148(12)	31(2)
C(19)	0.3498(3)	0.3800(5)	0.4150(3)	4.5(3)	C(55)	0.4341(10)	0.7912(13)	0.186(2)	27(2)
C(20)	0.1907(3)	0.5001(4)	0.4444(3)	3.9(3)	O(14)	0.3913(6)	0.6476(8)	0.0740(6)	20(1)
C(21)	0.1183(3)	0.5303(4)	0.4364(3)	4.1(3)	C(56)	0.3858(9)	0.5911(14)	0.0092(7)	21(1)
C(22)	0.0750(3)	0.4936(4)	0.3838(3)	3.8(3)	O(15)	0.0246(3)	0.2570(4)	0.3566(3)	12.3(4)
C(23)	0.0032(3)	0.5197(5)	0.3784(3)	5.0(4)					

$$^a B_{eq} = (8/3)\pi^2 \sum U_{ij} a_i^* a_j^* (\mathbf{a}_i \mathbf{a}_j)$$

Table III. Selected Bond Distances (\AA) and Bond Angles (deg) for [Ga(hbo)₂(O,O'-CH₃CO₂)]₂ with Estimated Standard Deviations in Parentheses

Bond Distances			
Ga(1)-O(2)	1.873(2)	O(3)-C(14)	1.255(2)
Ga(1)-O(3)	2.117(2)	N(1)-C(2)	1.411(3)
Ga(1)-N(1)	2.034(2)	N(1)-C(7)	1.303(3)
O(2)-C(9)	1.323(2)		
Bond Angles			
O(2)-Ga(1)-O(2')	109.7(1)	O(3)-Ga(1)-N(1')	92.87(7)
O(2)-Ga(1)-O(3)	155.67(7)	N(1)-Ga(1)-N(1')	175.8(1)
O(2)-Ga(1)-O(3')	94.60(7)	Ga(1)-O(2)-C(9)	127.2(1)
O(2)-Ga(1)-N(1)	88.64(7)	Ga(1)-O(3)-C(14)	90.3(2)
O(2)-Ga(1)-N(1')	88.93(7)	Ga(1)-N(1)-C(2)	130.4(1)
O(3)-Ga(1)-O(3')	61.1(1)	Ga(1)-N(1)-C(7)	123.4(1)
O(3)-Ga(1)-N(1)	90.76(7)	O(3)-C(14)-O(3')	118.2(4)

suffers from a disorder pertaining to the acetate methyl group from the crystallographically imposed C_2 axis of symmetry in the molecule. The geometry of [Ga(hbo)₂(O,O'-CH₃CO₂)]₂ is best described as quasi-octahedral. The main structural distortion is caused by the small bite angle of the acetate ligand (61.1(1)°), which is compensated for by an opening of the opposite O(2)-

Ga(1)-O(2') angle to 109.7(1)° (cf. Table III). The Ga-N bond distance in **2** (2.034(2) \AA) is comparable to the analogous bond lengths in the Ga(oz)₃ complex¹ (Ga-N bond distance range 2.028(2)-2.075(3) \AA). The Ga-O(2) bond length (1.873(2) \AA) is significantly shorter than its acetate counterpart (Ga-O(3) = 2.117(2) \AA). Although the phenolato oxygen, on the basis of the (negative) charge delocalization, should be the harder oxygen donor atom,²² the geometric factors are, in this case, of greater importance in accounting for the striking difference in the Ga-O bond lengths observed. In principle, the smaller the bite angle of a chelating ligand, the longer the M-L bond lengths. This well-known observation is also borne out by theoretical considerations (carried out specifically for five- and six-membered chelate ring geometries) which indicate that the aforementioned trend complies with the calculated minimum strain energy.²³ The

(22) Pearson, R. G. *Coord. Chem. Rev.* **1990**, *100*, 403 and references therein.(23) Hancock, R. D.; Martell, A. E. *Chem. Rev.* **1989**, *89*, 1875. The strain energy is alternatively (perhaps more aptly) referred to as the repulsion energy, viz. the repulsion between the M-L bonds.²⁴(24) Kepert, D. L. *Inorganic Stereochemistry*; Springer: New York, 1982; p 2.

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) for [Al(μ -OH)(hbo)₂]₂·4CH₃OH·H₂O (**3**) with Estimated Standard Deviations in Parentheses

Bond Distances			
Al(1)–O(2)	1.836(4)	Al(1)–O(4)	1.849(4)
Al(1)–O(9)	1.870(4)	Al(1)–O(10)	1.891(3)
Al(2)–O(6)	1.845(4)	Al(2)–O(8)	1.840(4)
Al(2)–O(9)	1.878(4)	Al(2)–O(10)	1.879(4)
Al(1)–N(1)	2.034(5)	Al(1)–N(2)	2.024(5)
Al(2)–N(3)	2.042(5)	Al(2)–N(4)	2.031(5)
Al(1)···Al(2)	2.966(2)		

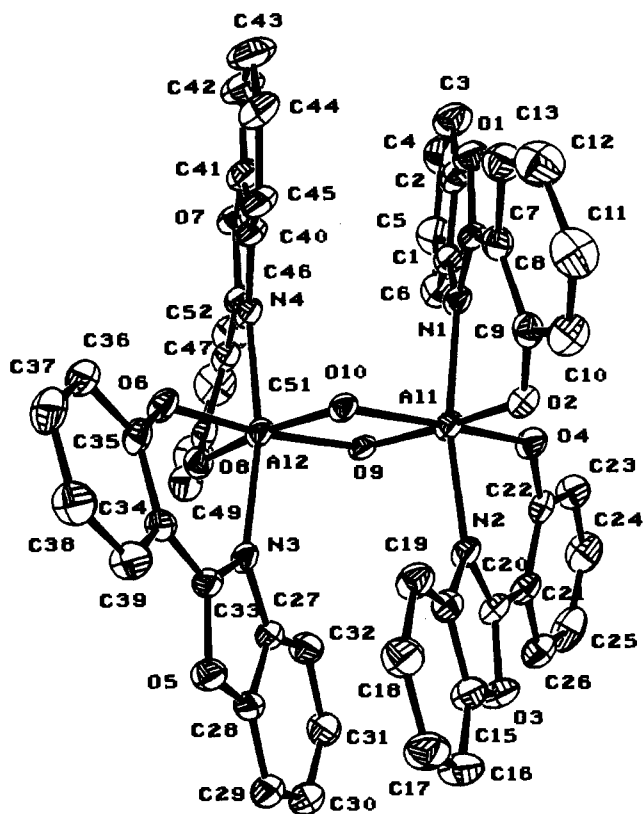
Bond Angles			
O(2)–Al(1)–O(4)	97.9(2)	O(2)–Al(1)–O(9)	169.4(2)
O(2)–Al(1)–O(10)	93.8(2)	O(2)–Al(1)–N(1)	86.6(2)
O(2)–Al(1)–N(2)	84.9(2)	O(4)–Al(1)–O(9)	92.7(2)
O(4)–Al(1)–O(10)	168.2(2)	O(4)–Al(1)–N(1)	86.9(2)
O(4)–Al(1)–N(2)	86.8(2)	O(9)–Al(1)–O(10)	75.7(2)
O(9)–Al(1)–N(1)	95.0(2)	O(9)–Al(1)–N(2)	94.7(2)
O(10)–Al(1)–N(1)	91.9(2)	O(10)–Al(1)–N(2)	96.2(2)
N(1)–Al(1)–N(2)	168.6(2)	O(6)–Al(2)–O(8)	96.2(2)
O(6)–Al(2)–O(9)	169.2(2)	O(6)–Al(2)–O(10)	93.9(2)
O(6)–Al(2)–N(3)	86.6(2)	O(6)–Al(2)–N(4)	85.1(2)
O(8)–Al(2)–O(9)	94.2(2)	O(8)–Al(2)–O(10)	169.8(2)
O(8)–Al(2)–N(3)	86.6(2)	O(8)–Al(2)–N(4)	86.9(2)
O(9)–Al(2)–O(10)	75.8(2)	O(9)–Al(2)–N(3)	96.9(2)
O(9)–Al(2)–N(4)	92.6(2)	Al(1)–O(9)–Al(2)	104.6(2)
Al(1)–O(10)–Al(2)	103.8(2)		

Ga–N bond distance lies in between the Ga–O_{phenolato} and the Ga–O_{acetato} bond lengths (*cf.* Table III).

The structure of [Al(μ -OH)(hbo)₂]₂·4CH₃OH·H₂O (**3**) and its atom-labeling scheme are shown in Figure 2. The CH₃OH and H₂O solvates have been omitted for the sake of clarity. Each of the Al centers is surrounded by two hbo⁻ and two hydroxo ligands in an almost octahedral geometry; the [Al₂(μ -OH)₂]⁴⁺ core is strictly planar. Furthermore, the Al–Al vector is a pseudo 2-fold axis. The oxazole ring nitrogens are *trans* to one another in both halves of the molecule. Selected bond distances and angles appear in Table IV. The Al···Al distance is 2.966(2) Å, and the Al–O bridge distances range from 1.870(4) to 1.879(4) Å. The Al–O–Al bridging angles are 103.8(2) and 104.6(2)°, and the O–Al–O angles are 75.7(2) and 75.8(2)°. These parameters are slightly different from the range of the core distances and angles for the four previously characterized bis(μ -hydroxo)-bridged dimers,^{14–17} which are as follows: Al···Al, 2.842–2.939 Å; Al–O–Al, 100.4–101.8°; O–Al–O, 78.2–79.6°. These differences probably reflect the steric bulk of the terminal ligands and are all consistent with this idea except that the Al–OH distances in **3** are within the reported range 1.816–1.923 Å. The Al–O phenolate distances in **3** range from 1.836(4) to 1.849(4) Å, and the Al–N distances range from 2.024(5) to 2.042(5) Å, within the range of the parameters reported for Al(oz)₃.¹

Solution NMR Studies. VT ¹H NMR experiments were carried out (in CDCl₃) to examine whether any (lower symmetry) geometric isomers of the [Ga(hbo)₂(O, O'-CH₃CO₂)] could be detected. Only *one* singlet signal for the acetate methyl group was observed (at *ca.* 1.7 ppm) throughout the temperature range examined (–50 to +50 °C), indicating that only the C₂-symmetric isomer is present in solution. This is not an unexpected finding given the stereochemical rigidity imposed by the less sterically demanding oz⁻ ligands in Ga(oz)₃.¹ Moreover, the room temperature ¹³C NMR clearly indicated the one set of aromatic signals expected in a C₂-symmetric arrangement of the ligands about the metal ion. On the basis of this NMR evidence, it is tenable to suggest that the structure observed in the solid state (Figure 1) is conserved in solution.

The ¹H NMR of [Al(μ -OH)(hbo)₂]₂·4CH₃OH·H₂O (in CDCl₃) showed a singlet at 11.47 ppm which was assigned to the μ -OH protons. The ²⁷Al NMR of **3** in CDCl₃ showed a signal at 5 ppm

**Figure 2.** ORTEP view of [Al(μ -OH)(hbo)₂]₂.

with a large $W_{1/2}$ (2.0 kHz). Both of the ²⁷Al NMR spectral features compare well with those of Al(oz)₃ complexes.¹ The larger $W_{1/2}$ value observed for this Al complex is indicative of a lower symmetry about the metal center.²⁵ On the basis of the NMR data, the solution structure of this Al complex in CDCl₃ is consistent with that found in the solid state.

Concluding Remarks. The Al and Ga complexes of the bulky ligand 2-(2'-hydroxyphenyl)-2-benzoxazole have been synthesized and characterized. Two different and uncommon coordination geometries of these two group 13 metal ions were stabilized in the solid state and in solution as evinced by X-ray crystallography and NMR (VT ¹H NMR, ¹³C, ²⁷Al) spectroscopy. Therefore, this ligand system provides an interesting example of an intricate balance between the steric demands of the ligand and the coordination requirements of the metal, such that substantially different structural entities are formed with the two group 13 congeners.

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Supplementary Material Available: Complete tables of crystallographic data, bond distances, and bond angles and tables of hydrogen atom coordinates, anisotropic thermal parameters, torsion angles, intermolecular contacts, and least-squares planes for each of the two structures (46 pages). Ordering information is given on any current masthead page.

(25) The ²⁷Al NMR line width ($W_{1/2}$) can vary from 3 Hz to several kHz, depending on a number of factors that affect the quadrupolar relaxation of the aluminium nucleus ($Q = 0.149 \times 10^{-24}$ cm²), most significantly, the symmetry about the metal center.²⁶

(26) Akitt, J. W. *Prog. NMR Spectrosc.* 1989, 21, 1.